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ANALYSIS OF MIDDLE DISTILLATE FUELS BY FIELD IONIZATION MASS SPECTROMETRY

Interim Technical Report
Covering Period from September 7, 1979
through September 9, 1980

By: S. E. Buttrill, Jr.
Manager
Mass Spectrometry Development Program

Sept. 1980

Prepared for:

Robert N. Hazlett
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SRI Project PYU 8903

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ABSTRACT

This interim technical report describes work completed during the first twelve months of a research program to develop field ionization mass spectrometry for quantitative analyses of middle distillate fuels. The relative field ionization sensitivities were measured for 90 compounds typical of those which might be found in middle distillate fuels produced from petroleum, shale, or coal. The FIMS sensitivities for naphthalenes are from 2 to 3 times greater than for saturates, an advantage for detecting these minor components. Sensitivity was also high for nitrogen and sulfur containing compounds which will increase the level at which these materials may be detected in fuels. Distillation of the fuel sample from a solids probe into the FIMS source was found to not provide sufficient separation of compounds such as naphthalenes and saturates. These compounds will be separated using high resolution FIMS. The precision of the proposed analysis method was evaluated with an authentic jet fuel sample, and it was found that the coefficient of variation of minor components averaged 6 percent while that of larger components was 2 or 3 percent. The use of high resolution FIMS together with a batch inlet system and computerized data collection and analysis system appears to be a highly promising technique for providing detailed quantitative data on the chemical composition of middle distillate fuels.

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INTRODUCTION

As supplies of both domestic and imported petroleum become increasingly costly and less readily available, our nation's security requires the development of alternative sources of mobility fuels. Shale and coal are the leading condidates to provide dependable domestic sources of middle distillate fuels. Fuels derived from these alternate sources are very complex mixtures containing hundreds of different compounds. Basic research aimed at understanding and predicting the performance and stability of alternate fuels requires new analytical methods to give accurate, quantitative, and rapid information on the amounts and types of the different compounds present in a fuel sample. This information will then be correlated with the physical properties, combustion performance, and stability characteristics of the fuel to determine which chemical compounds are responsible for particular fuel characteristics. The purpose of this project is to apply SRI International's unique field ionization mass spectrometry (FIMS) expertice to develop improved methods of rapidly, accurately, and routinely obtaining the required detailed analyses of middle distillate mobility fuels.

Most of the Navy's mobility fuel requirements are met by JP-5 and diesel fuel marine. FI mass spectrometric analysis procedures for these fuels are being developed on this project to provide the following information on the composition of these fuels.

- Types and amounts of hetero atom compounds. These are important in fuel stability, combustion, and toxicity.
- Types and amounts of aromatic hydrocarbons. These are important in the combustion, toxicity, peroxidation, and stability.

- Amounts of normal alkanes and other symmetrical molecules. These are important in determining the freezing point of the fuel.
- Types and amounts of polyaromatic hydrocarbons. These are important in determining the combustion and peroxidation properties of the fuel.

As a result of work completed thus far during the first phase of this program, the following analysis procedure is anticipated. Samples of liquid fuel will be vaporized into a glass batch inlet system for a field ionization mass spectrometer. Because all of the fuel sample is vaporized, the composition of the gas mixture entering the FIMS is constant, making it possible to accumulate and average as many spectra as necessary in order to obtain the desired dynamic range and quantitative accuracy. The mass spectrometer will be operated at high resolving power so that the molecular ions for the individual fuel components can be separated. Accurate mass measurements of these ions will allow the elemental composition (chemical formula) to be determined, even if the precise structure remains ambiguous. Use of measured relative field ionization efficiencies together with the elemental composition of the molecular ions will allow the conversion of the relative field ionization signals for each compound into the mole fraction of that compound present in the fuel sample. This capability for such highly detailed analyses of fuel samples is unprecedented and should prove to be extremely valuable in studies which correlate fuel quality and performance with chemical composition. In order to facilitate these correlations, a sophisticated data system will be needed to convert the detailed composition data into summaries of the total amounts of various types of compounds present in the fuel.

This report describes the work completed during the first twelve months of this project, and presents the reasoning which led to the above analysis procedure. The report concludes with a discussion of the details of the projected capabilities of the high resolution field ionization mass spectrometer system.

INSTRUMENTATION AND MATERIALS

Field Ionization Mass Spectrometry (FIMS)

Analysis by mass spectrometry involves three principal steps. First, the sample of liquid or solid is vaporized and introduced into the mass spectrometer at a pressure usually less than 10^{-5} torr. At this low pressure, the molecules of the sample do not interact with each other; hence, the mass spectrum of the mixture is just the sum of the spectra of each of its components. Secondly, the sample molecules are converted into ions by any one of a number of processes. In this project, SRI's unique volcano style field ionization source is used to produce unfragmented molecular ions by field ionization, as discussed below. Finally, the ions are separated according to mass. The relative numbers of ions detected are recorded as a function of mass to produce the mass spectra. For the work reported here, the mass analyzer was a 90° single focusing, ten inch radius, magnetic sector.

Of all the ionization techniques used in mass spectrometry, field ionization is unique in its ability to produce unfragmented molecular ions from almost all organic compounds. Field ionization can occur when molecules are exposed to very high electric field strengths, of the order of 10^8 V/cm. Under these conditions, an electron may tunnel from the molecule to the field emitter producing a molecular ion. When laboratory voltages of a few kilovolts are used, very sharply pointed emitters are required to produce the necessary high field strengths.

The early version of the volcano type field ionization source is described in the publication by Aberth and Spindt.* This ionizer was used in the early work on this project, but was replaced by the improved volcano style source assembly shown in Figure 1. The focus electrode has been removed from the source for clarity. Important new features include the large ceramic base, which provides space for mounting all the required electrical connections. The sturdy lead support posts prevent stress from being placed on the relatively fragile grid heater. The new design also provides increased physical strength and structural rigidity. Also, the grid mount was redesigned to simplify the alignment of the volcano aperture with one of the openings in the counter electrode grid.

Figure 2 shows a scanning electron micrograph of the new source at approximately 20 times actual size. The grid and grid holder are clearly visible. The entire volcano, which is clamped to its support pillar, can be seen through the grid. In Figure 3, the volcano structure, shown at approximately 170 times actual size, is now clearly visible. Figure 4 shows that the volcano throat is precisely centered beneath one of the grid openings. The diameter of the base of this volcano is approximately 100 micrometers, whereas the diameter of the rim is approximately 18 micrometers. The distance between grid lines is 100 micrometers, and by comparison, the volcano rim is approximately 25 micrometers away from the counter electrode grid. A potential difference of 2.0 kV between the volcano and the counterelectrode yields an average field strength of 8×10^7 V/m. This field strength in itself is not high enough to induce field ionization. However, as shown in Figure 5, the rim of the volcano

* W. Aberth and C. A. Spindt, Int. J. Mass Spectrom. Ion Phys., 25, 183 (1977).



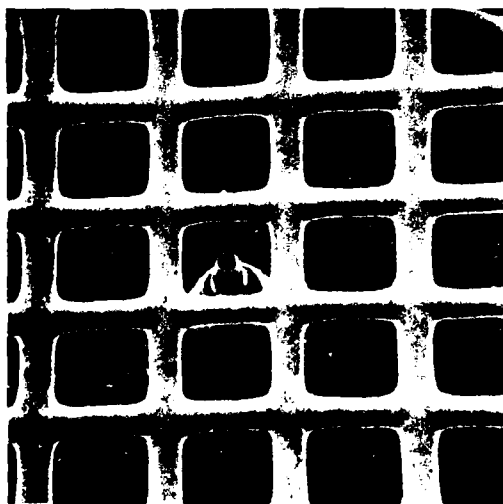
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FIGURE 1 IMPROVED VOLCANO TYPE FIELD
IONIZATION SOURCE ASSEMBLY SHOWN
WITH FOCUS LENS ELEMENT REMOVED



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FIGURE 2 SCANNING ELECTRON MICROGRAPH (SEM) OF THE IONIZER ASSEMBLY SHOWING THE VOLCANO IONIZER MOUNTED BELOW THE GRID COUNTER ELECTRODE. ABOUT 20 X.



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FIGURE 3 SEM OF THE VOLCANO AND GRID AT ABOUT 170 X.



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FIGURE 4 SEM SHOWING THE VOLCANO RIM
CENTERED IN ONE OPENING IN THE
GRID

The grid spacing is 10 lines per millimeter.
About 450 X.



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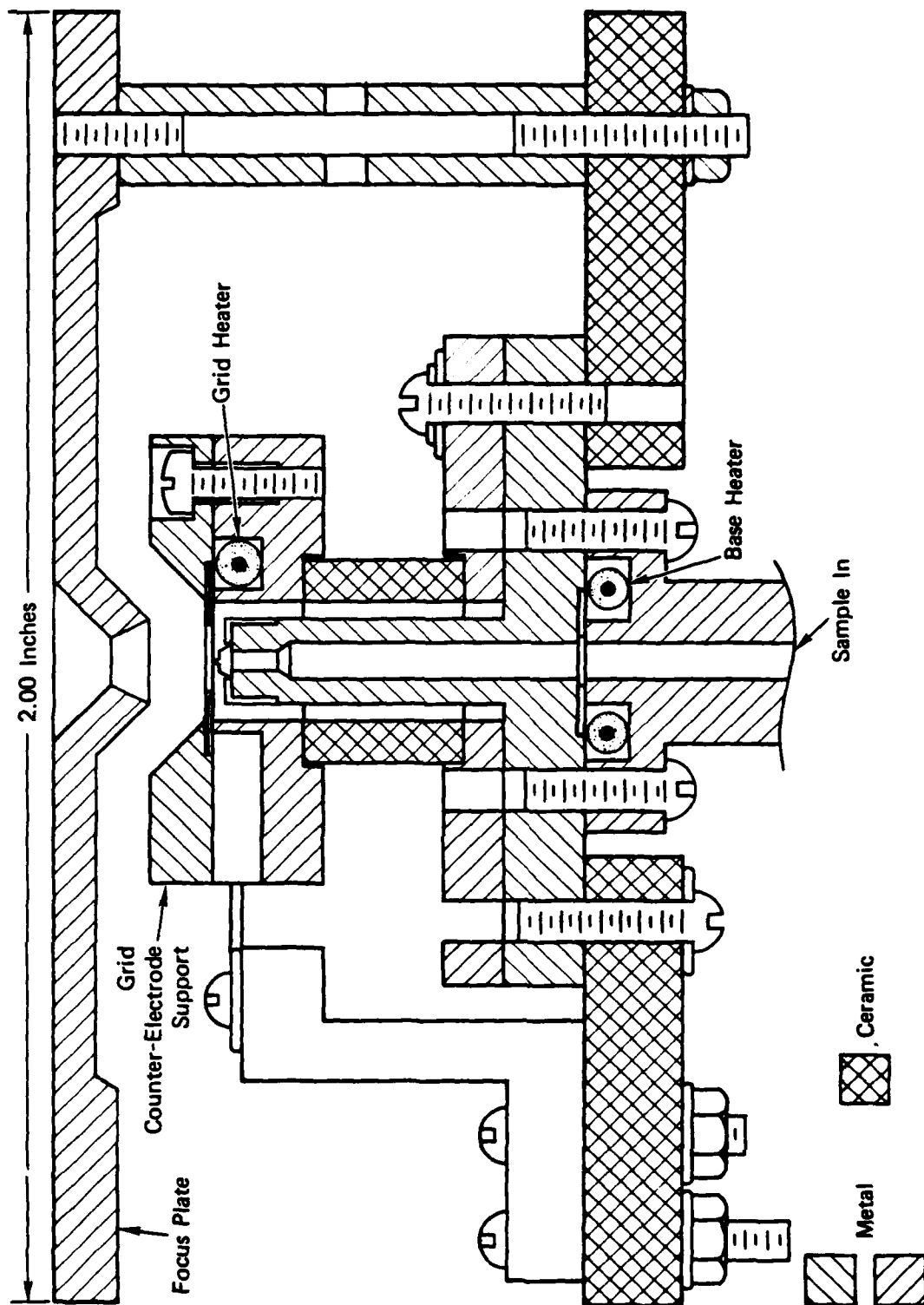
FIGURE 5 SEM OF THE VOLCANO RIM SHOWING
THE PRESENCE OF CARBON DENDRITE
ACTIVATION

The diameter of the carbon whiskers is
400 Å or less. About 5800 X.

is covered with extremely fine dendrite structures formed when the source is first run in the test system. The fine structure in these dendrites is less than 400 Angstroms in diameter and is not resolvable with this scanning electron microscope. Because the demensions of the dendrite whiskers are not known, the local field strength cannot be estimated. However, the electric field strength near the sharply pointed structures is high enough to cause extensive field ionization.

A scale drawing of a cross section of the new ion source is shown in Figure 6. The sturdy focus electrode plate on the top of the source, which was not shown in the scanning electron micrographs, provides a strong protective cover for the relatively delicate grid structure and the volcano. The focus electrode also serves as an alignment reference for mounting the source. The focus electrode plate is exactly 2.000 inches in diameter with the shaped focusing aperture in its exact center. When the source is assembled, the focus electrode is optically aligned with the opening in the volcano. Thus, the focused ion beam will be formed along an axis passing through the center of the focus electrode. The source is mounted on the mass spectrometer by clamping the focus electrode into a plate with a matching 2 inch diameter depression. It is thus possible to remove and replace an entire ion source assembly and retain alignment of the volcano with the axis of the ion optical system.

Figure 6 also shows that sample molecules entering the source from the bottom may escape only by passing through the opening in the volcano itself. It is this aspect of the volcano source design that is thought to be largely responsible for its high sensitivity compared with the more widely used activated wire and razor blade field ionization sources. Sample molecules may be introduced into the source from either a conventional solids probe or from a batch inlet system (see below).



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FIGURE 6 IMPROVED VOLCANO TYPE FIELD IONIZATION SOURCE

Although not shown explicitly in Figure 6, either of these two methods of sample introduction may be used easily with the improved volcano ion source assembly.

Batch Inlet System

In order to introduce volatile fuels and mixtures of test compounds into the field ionization source, a new glass batch inlet system was designed and built. Figure 7 shows the schematic diagram of this new inlet system, which is based on a 0.5 liter glass bulb. The entire batch inlet is contained within an aluminum oven which can be heated to a temperature of up to 180°C. Provision is made for evacuating the batch inlet by means of a mechanical vacuum pump. A trap packed with activated molecular sieve prevents mechanical pump oil vapors from entering the batch inlet system. Samples of 1-10 microliters of fuel or other organic liquids are injected into the evacuated inlet system through a high temperature septum, similar to the injectors used on gas chromatographs. The resulting pressure of volatilized organic compounds in the batch inlet is between approximately 0.5 and 5 torr. The flow rate through the 0.003 inch ID glass capillary is so small that the pressure inside the expansion bulb remains effectively constant for several hours, and the field ionization source receives a constant flow of sample. Furthermore, the amount of a particular fuel component reaching the ion source is proportional to the amount of that component originally present in the fuel sample.

Use of the glass batch inlet system for analysis of middle distillate fuels has several advantages. First, the fact that a constant signal is simultaneously available from all components in the fuel makes it possible to average many mass spectrometer scans. Within the limits of the present mass spectrometer data system, spectra can be averaged

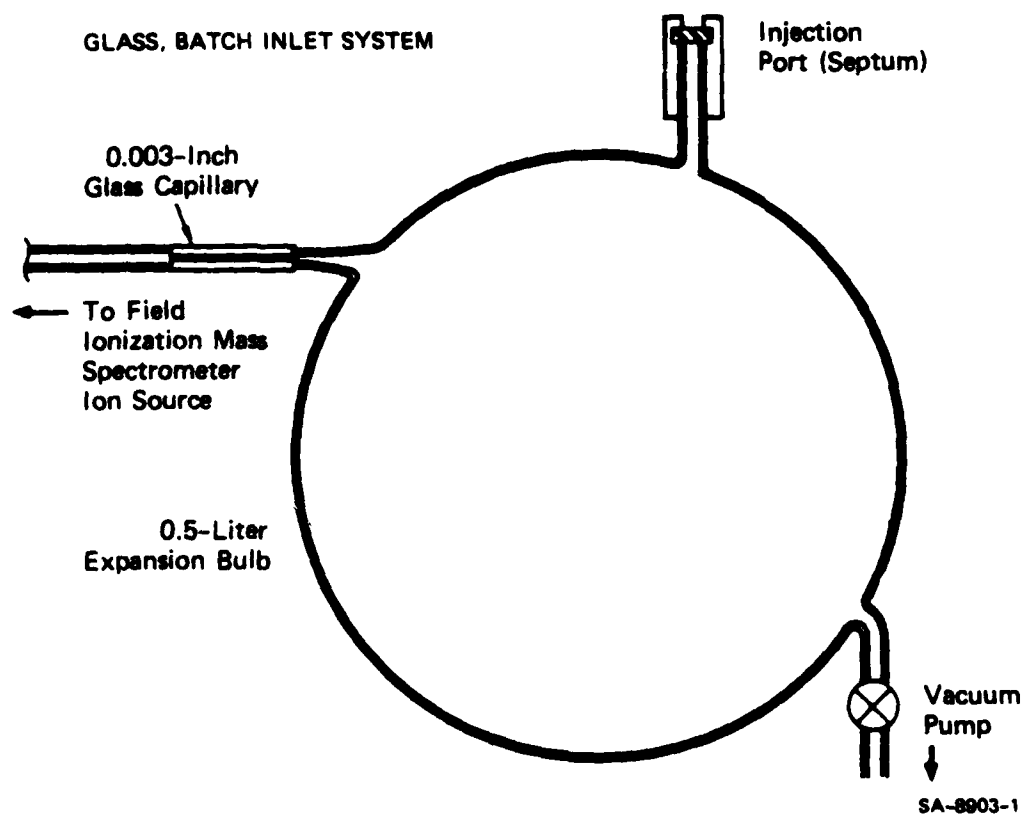


FIGURE 7 SCHEMATIC DIAGRAM OF THE ALL-GLASS HEATED BATCH INLET SYSTEM BUILT TO INTRODUCE VOLATILE FUEL SAMPLES INTO THE FIELD IONIZATION MASS SPECTROMETER

until any required degree of precision is obtained. Second, because a relatively large amount of fuel is injected from a syringe directly into the inlet system, loss of volatile components of the sample is avoided. This makes it possible to accurately determine compounds such as octanes and nonanes which suffer some unavoidable loss when the sample is introduced by means of the normal solids probe. Finally, because the inlet system is constructed entirely of glass, loss or reaction of sample components on the surfaces of the inlet system is minimized.

FIELD IONIZATION EFFICIENCY MEASUREMENTS

Objective

Although the field ionization efficiencies of most compounds are similar, exact ionization efficiency measurements of the types of compounds expected in middle distillate fuels are required in order to convert a field ionization mass spectrum into a quantitative analysis of the fuel. In this part of the project, the field ionization efficiencies of 90 compounds were measured relative to the field ionization efficiency of toluene.

Method

Mixtures of 8-12 pure compounds were prepared by weight for analysis by FIMS. The mixtures were stored in one milliliter vials equipped with caps containing built in Teflon slide valves. These valves allowed samples to be removed with a syringe without actually opening the sample container to the atmosphere, thus reducing losses of the volatile components. The sample taken up in the syringe was injected directly into the evacuated batch inlet system. Field ionization mass spectra were collected using the PDP 11/10 computer system. In most cases, three separate injections were made of each mixture, and if a good agreement was obtained, the results for the three runs were averaged. The batch inlet system was operated at 150°C for all runs.

Results

The relative field ionization sensitivities for 90 compounds are given in Tables 1-6. Compounds are grouped into tables according to their z value, where z is determined from the chemical formula of the compound when it is expressed in the form C_nH_{2n+z} . Table 1 shows the relative FIMS sensitivities measured for 18 alkanes. The sensitivities relative to toluene range from a low of 0.26 for hexane and 3-methylhexane up to 0.51 for n-dodecane. The values for the branched hydrocarbons are generally lower than for the normal alkanes and there seems to be more scatter in the values of the sensitivities for the lighter hydrocarbons. We believe that at least some of this variability is caused by uncontrollable loss of these more volatile components from the test mixtures. The sensitivities reported are based on the intensity of the molecular ion alone. While the normal alkanes yield only molecular ions on field ionization, the branched alkanes do form some fragment ions. The intensities of these fragments are not included in the calculations of the FIMS sensitivity. If they were, the sensitivities of the branched alkanes would be closer to those of the normal alkanes. Additional branched alkanes will be examined during the next phase of this project.

Table 2 shows the relative FIMS sensitivities of 8 cycloalkanes. As would be expected, their sensitivities are essentially equivalent to those of the alkanes shown in Table 1. Additional cycloalkanes were not available to us at the time the field ionization sensitivities were being measured. However, we have since acquired 12 additional cyclohexanes from NRL and the Chemical Sample Company. These compounds will be included in the next set of sensitivity measurements.

Table 1

RELATIVE FIMS SENSITIVITIES OF ALKANES

n	Compound	$C_n H_{2n+2}$	Rel. Sens.
		MW	
6	n-Hexane	86	0.26
	2-Me-Pentane		0.44
	3-Me-Pentane		0.27
	2,3 DiMe-Butane		0.32
7	n-Heptane	100	0.41
	3-Me-Hexane		0.26
	2-Me-Hexane		0.33
8	n-Octane	114	0.46
	2-Me-Heptane		0.35
	2,5-DiMe-Hexane		0.34
9	n-Nonane	128	0.41
10	n-Decane	142	0.41
11	n-Undecane	156	0.46
12	n-Dodecane	170	0.51
13	n-Tridecane	184	0.50
14	n-tetradecane	198	0.44
15	n-Pentadecane	212	0.44
16	n-Hexadecane	226	0.44

Table 2

RELATIVE FIMS SENSITIVITIES OF CYCLOALKANES

		$C_n H_{2n}$	
n	Compound	MW	Relative Sensitivity
6	Cyclohexane	84	0.46
	Me-Cyclopentane		0.29
7	Cycloheptane	98	0.44
	Me-Cyclohexane		0.37
8	Cyclooctane	112	0.53
	1,4 DiMe-Cyclohexane		0.61
	Ethylcyclohexane		0.56
9	Isopropylcyclohexane	126	0.50

Table 3 gives the relative FIMS sensitivities measured for 24 aromatic compounds including toluene, the reference compound. In general, the sensitivities for aromatic compounds are 2 to 3 times greater than those for saturated hydrocarbons. The sensitivities for the substituted benzenes seem to reach a maximum between C9 and C10. The apparent decrease in sensitivity for the series of 1-phenylalkanes above C14 may reflect a failure of these heavier compounds to completely vaporize within the batch inlet system. Our first measurements for these compounds were low for this reason, and even at 150°C, these compounds may absorb more strongly on the surface of the inlet system and thus not be entering the ion source at the rate expected. However, all of these compounds have a vapor pressure over 1 torr at 150°C. Nonetheless, it may be necessary to increase the operating temperature of the batch inlet system in order to accurately quantitate compounds above C15.

The relative FIMS sensitivities for naphthalenes and diaromatics are shown in Table 4. The sensitivities measured for the few naphthalenes which were commercially available are about 20% higher than the sensitivities measured for aromatic molecules of comparable size. The value of 1.48 obtained for 2-methylnaphthylene is the highest sensitivity found for any hydrocarbon measured. The high sensitivity for naphthalenes relative to alkanes will be an advantage when actual fuel analyses are begun, because the naphthalenes are normally present in much lower concentrations than the saturates, which are the major components of most fuels.

The FIMS sensitivities for diaromatics (C_nH_{2n-14}) shown in Table 4 range from a high of 1.32 for biphenyl to a low of 0.88 for 2,2-diphenylpropane. This last value may be low because of the low volatility of the diphenylpropane.

Table 3

RELATIVE FIMS SENSITIVITIES FOR AROMATICS

		$C_n H_{2n-6}$	
n	Compound	MW	Rel. Sens.
6	Benzene	78	0.88
7	Toluene	92	1.00*
8	Xylenes	106	1.12
	Ethylbenzene		1.04
9	Mesitylene	120	1.22
	O-ethyltoluene		1.29
	p-ethyltoluene		1.25
	n-propylbenzene		1.18
	isopropylbenzene		1.24
10	p-isopropyltoluene	134	1.23
	diethylbenzenes		1.19
	isobutylbenzene		1.17
11	pentamethylbenzene	148	1.12
	1,3 diethyl-5-Me-benzene		1.18
	p-t-butyltoluene		1.26
	n-pentylbenzene		1.08
12	1-phenylhexane	162	1.18
13	1-phenylheptane	176	1.18
14	p-di-t-butylbenzene	190	1.36
	1-phenyloctane		1.09

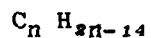
Table 3 (continued)

	Compound	MW	Rel. Sens.
15	1,3,5 tri-isopropylbenzene	204	1.29
	1-phenylnonane		0.96
16	1-phenyldecane	218	0.94
18	1-phenyldodecane	246	0.88
19	1-phenyltridecane	260	0.88

Table 4

RELATIVE FIMS SENSITIVITIES FOR
NAPHTHALENES AND DIAROMATICS

n	Compound	MW	Rel. Sens.
10	Naphthalene	128	1.42
11	2 Me-Naphthalene	142	1.48
12	2 Ethyl Naphthalene	156	1.42
	DiMe Naphthalene		1.23
13	2,3,5 TriMe Naphthalene	170	1.22

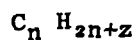


n	Compound	MW	Rel. Sens.
12	Biphenyl	154	1.32
13	Diphenylmethane	168	1.07
	4-phenyltoluene		1.28
14	Bibenzyl	182	0.99
	3,3'DiMe-Biphenyl		1.08
15	2,2 Diphenylpropane	196	0.88

Table 5 summarizes the relative field ionization sensitivities of 19 hydrocarbons of various z number. The relative sensitivities for the saturated 2 and 3 ringed compounds are comparable to those for monocycloalkanes (Table 2) of similar molecular weight. As would be expected, compounds containing aromatic rings have sensitivities similar to those of other aromatic compounds (Table 3).

Table 6 shows the relative FIMS sensitivities of 9 compounds containing sulfur or nitrogen. Molecules containing these heteroatoms are thought to exert a strong influence on the stability and toxicity of alternate fuels. Their presence also produces undesirable emissions when the fuels are burned. With the exception of thiophene, the relative sensitivities of these compounds are all significantly higher than those of hydrocarbons of corresponding molecular weight. This is a very fortunate situation, since compounds containing these heteroatoms are expected to be present in very low concentrations in most finished fuels. The increased sensitivity for these compounds will make it possible to detect them at lower levels than will be achievable for hydrocarbons.

Table 5

RELATIVE FIMS SENSITIVITIES OF
OTHER HYDROCARBONS

z	n	Compound	MW	Rel. Sens.
-2	7	Norbornane	96	0.29
	9	Hexahydroindan	124	0.54
	10	Decalin	138	0.78
	12	Dicyclohexyl	166	0.74
-4	10	Adamantane	136	0.68
		Camphene		0.76
		Pinene		0.57
	12	1,3-Dimethyladamantane	164	0.67
	13	Perhydrofluorene	178	0.62
	15	1-Phenyl-3,4-dihydronaphthalene	206	0.92
-8	9	Cyclopropylbenzene	118	1.30
		Indan		1.25
	10	α -Cyclopropyltoluene	132	0.89
		Tetralin (1,2,3,4-tetrahydronaphthalene)		1.34
	12	Cyclohexylbenzene	160	1.12
-10	10	1,2-Dihydronaphthalene	130	1.44
-16	12	Acenaphthalene	152	1.09
	13	Fluorene	166	1.11
-20	16	1-Phenylnaphthalene	204	0.81

Table 6

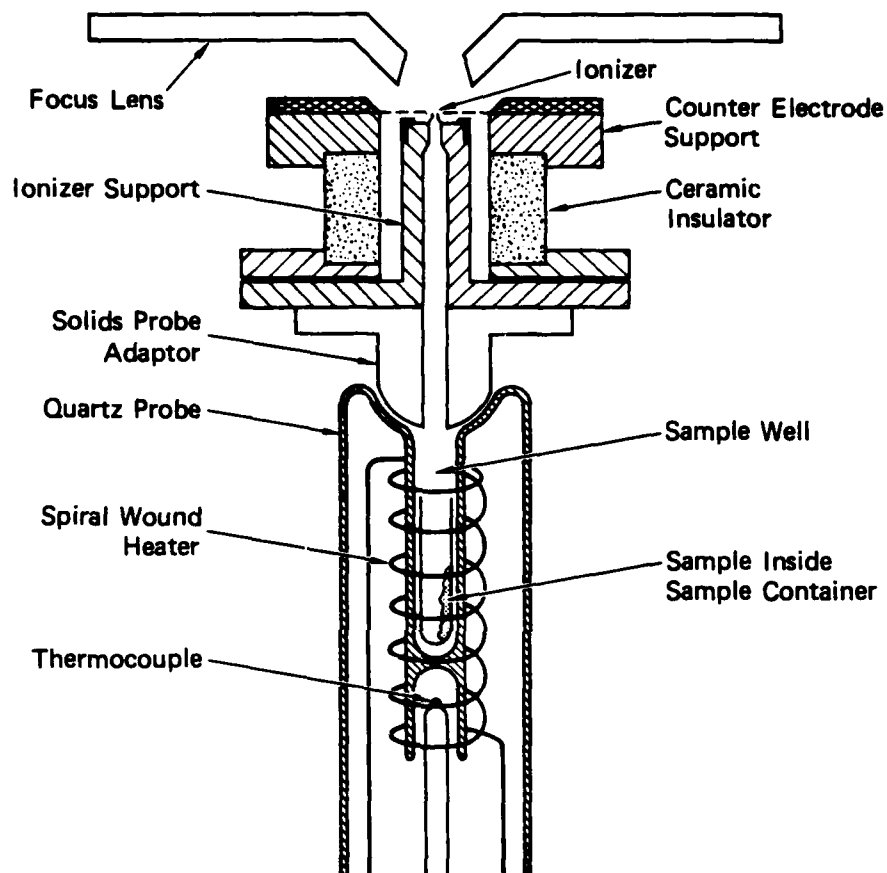
RELATIVE FIMS SENSITIVITIES OF SOME
SULFUR AND NITROGEN COMPOUNDS

Compound	Formula	MW	Relative Sensitivity
Thiophene	C_4H_4S	84	0.67
Thianaphthene	C_8H_6S	134	1.62
n-Butyldisulfide	$C_8H_{18}S_2$	178	2.67
n-Hexyl Sulfide	$C_{12}H_{26}S$	202	2.18
Pyrrole	C_4H_5N	67	1.88
Indole	C_8H_7N	117	2.28
Collidine	$C_8H_{11}N$	121	2.25
Quinoline	C_9H_7N	129	2.28
Tetrahydroquinoline	$C_9H_{11}N$	133	3.54

IMPROVED PROBE DISTILLATION

At the present time we are using a single focusing mass spectrometer for the field ionization analysis of fuel samples. This instrument and the PDP-11/10 data system are capable of determining the masses of molecular ions with an accuracy of ± 0.2 mass units. Middle distillate fuels contain mixtures of hydrocarbon types, and some of these different types have molecular weights which fall in the same series. Probably the most important pair of compound classes which have the same nominal molecular weights are the saturates (C_nH_{2n+2}) and the naphthalenes (C_nH_{2n-12}). For example, decane, $C_{10}H_{22}$, has an exact molecular ion with an exact molecular weight of 142.0783 whereas methylnaphthalene, $C_{11}H_{10}$, has an exact molecular weight of 142.0783, a difference of 0.0939 mass units. Our single focusing mass spectrometer is not capable of resolving these two components, so it was desirable to explore methods of analyzing fuel samples which involved a separation of the naphthalenes and saturates.

In previous work for the Naval Research Laboratory, we analyzed numerous distillate fuel samples by introducing them into the field ionization mass spectrometer using a conventional solids probe. This method of analyzing samples is shown schematically in Figure 8. For liquid samples such as fuels, it is necessary to freeze the sample into the solids probe before exposing it to the vacuum system of the mass spectrometer. As the frozen sample is slowly heated up, various components of the fuel evaporate and enter the volcano style field ionization source, where they are converted into ions and subsequently mass analyzed and detected. The more volatile compounds evaporate at lower temperatures, and the heavier and less volatile components evaporate at higher temperatures. It is possible to obtain a significant degree of



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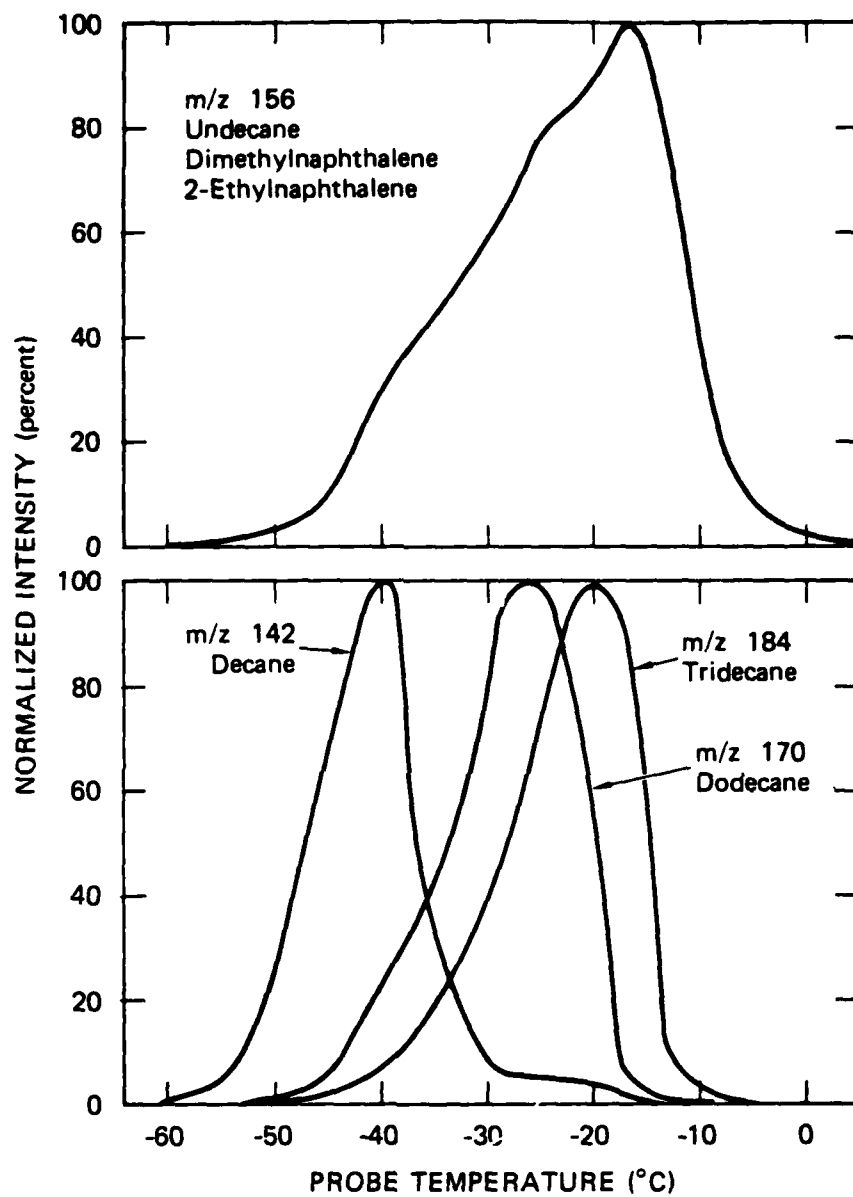
FIGURE 8 SCHEMATIC DIAGRAM OF THE METHOD OF ANALYZING SOLID SAMPLES USING THE VOLCANO STYLE FIELD IONIZATION SOURCE

separation of different compounds by means of a careful distillation of the sample from the probe into the mass spectrometer ion source. Using the arrangement shown in Figure 8, this process is a simple one stage vacuum distillation.

The purpose of this phase of the research effort was to test the feasibility of using different packing materials within the probe to increase the number of effective stages in the distillation and therefore the degree of separation of various components in the fuel. The separation of naphthalenes from saturates hydrocarbons of the same nominal molecular weight was chosen as a test case. A standard test mixture was prepared which contained decane, undecane, dodecane, tridecane, as well as dimethylnaphthalene and 2-ethylnaphthalene.

In order to establish a baseline for judging the performance of various probe packing materials, a distillation of this hydrocarbon mixture into the field ionization mass spectrometer was performed using the normal solids probe procedure, as diagramed in Figure 8.

A sample of the test mixture was placed on the solids probe and frozen to dry ice temperature (-75°C). The probe was then introduced into the mass spectrometer vacuum and mated with the volcano style field ionization source. As the probe was slowly warmed up to room temperature, the mass spectrometer was scanned from mass 50 up to mass 350, with each scan being recorded and stored by the PDP 11/10 computerized data system. The molecular ion signals for each of the mixture components were then normalized to 100% at their maximum value and plotted as a function of probe temperature (Figure 9). In the absence of any probe packing material, the signal from decane reaches a maximum at a probe temperature of -40°C . The signal from the molecular ion of tridecane at m/z 184 reaches a maximum at a probe temperature of -20°C . In other words, the difference in maximum signals for the C10 and C13 hydrocarbons is only



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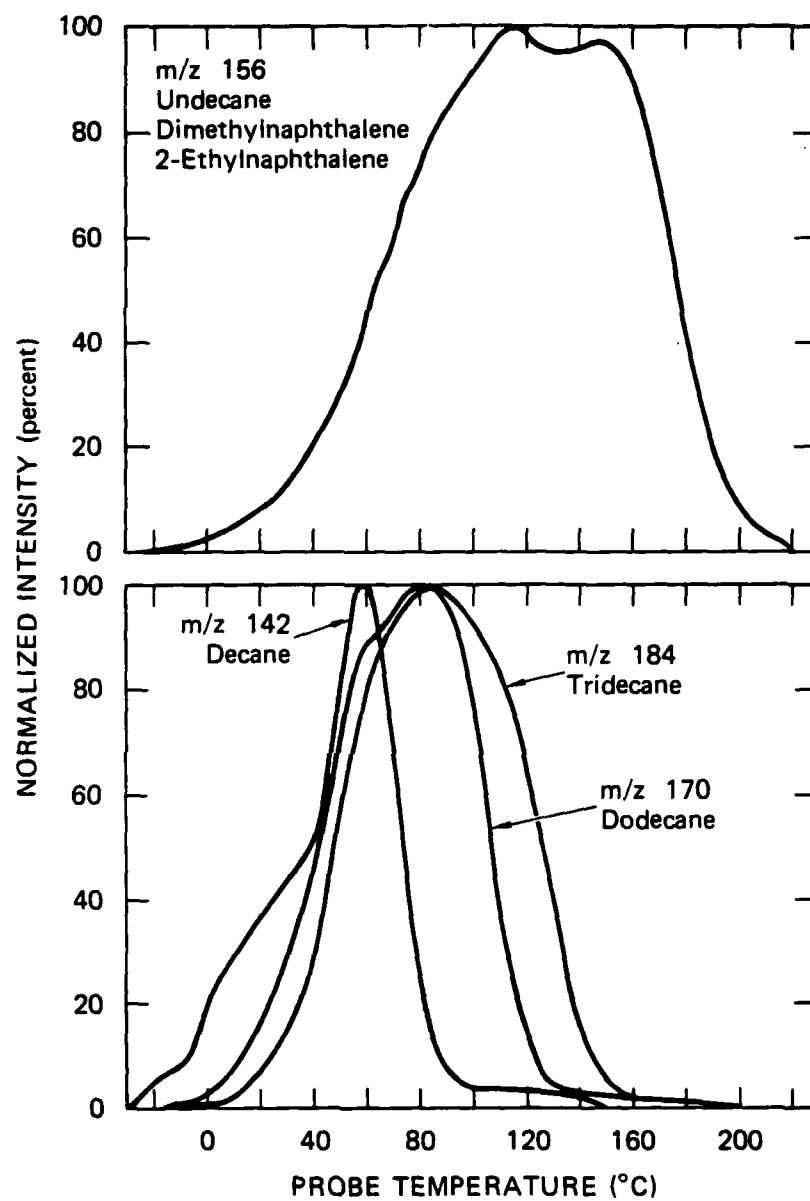
FIGURE 9 DISTILLATION OF HYDROCARBON MIXTURE FROM SOLIDS PROBE
ALONE INTO F1 MASS SPECTROMETER

20° apart. As shown in the lower plot in Figure 9, the individual alkane components are separated, but not resolved. They are easily distinguished however because they each have a different molecular weight. The test mixture contained 3 compounds with nominal molecular weight of 156: undecane, dimethylnaphthalene, and 2-ethylnaphthalene. The plot of the signal at this mass versus temperature is shown in the upper plot in Figure 9. Although there is a suggestion of 3 different components to this broad peak, the three components are not at all resolved from each other and it would not be practical to attempt to quantitate them on the basis of this separation.

Two different packing materials were tried for the probe in an attempt to improve the resolution of the probe distillation. These materials were Pyrex glass wool and microporous glass beads. The following procedure was used for both materials. The sample container was packed with the material, placed in the solids probe without any hydrocarbon mixture, and introduced into the mass spectrometer vacuum system. The probe and packing material was then baked to 350°C in vacuum to remove any traces of organic material which might cause spurious signals. When the packing material was clean, as judged by the absence of any material evolving from the probe and detectable by field ionization mass spectrometry, the probe was cooled and removed from the vacuum system. The test mixture was then applied to the bottom of the packed capillary using a micro syringe. The sample was frozen at dry ice temperature and introduced into the mass spectrometer in the normal way. Spectra were again recorded as a function of probe temperature until the sample was completely evaporated.

Somewhat surprisingly, the results for probe sample containers packed with Pyrex glass wool were indistinguishable from those shown in Figure 9 for the unpacked sample container. However, this result can be understood in terms of the long mean-free-path of molecules in the high vacuum of the mass spectrometer. The sample pressure inside the probe and volcano style field ionization source is estimated to be no more than 10^{-4} torr, and is quite possibly lower. At these pressures, sample molecules in the gas phase collide only with the walls of the sample container and packing material. The probability of collisions between gas phase sample molecules is extremely low. As a result, sample molecules, once vaporized, move rapidly through the packing material. They leave the probe and enter the ion source without ever reequilibrating with liquid phase sample. Thus, the presence of the packing material increases the number of collisions between surface and sample, but it does not provide any increase in the effective number of stages of distillation.

The second material tested as a packing for the probe sample holder was microporous glass beads. The glass beads were held in the sample container by a 2 millimeter plug of Pyrex glass wool. The packed sample container was baked out in vacuum at 350°C as described for the glass wool alone. The results of the probe distillation of the hydrocarbon test mixture from the microporous glass beads are shown in Figure 10. Notice that the temperature scale is compressed by a factor of 4 compared to Figure 9. The major effect of the glass beads is to increase the temperature at which the test compounds are vaporized into the ion source. The decane signal reaches a maximum at a probe temperature of approximately 60°C using the glass beads compared to -40°C using the unpacked sample holder or a sample holder packed with glass wool. The maximum signal for tridecane occurs at approximately 85°C with the microporous glass beads compared to -20°C for the unpacked probe. The difference in the



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FIGURE 10 DISTILLATION OF HYDROCARBON MIXTURE FROM POROUS GLASS BEADS INTO F1 MASS SPECTROMETER

temperatures at which the maximum in these two peaks occur has been increased by about 5°C by the glass beads, but as can be seen clearly from the lower plot in Figure 10, the resolution of the distillation has actually decreased.

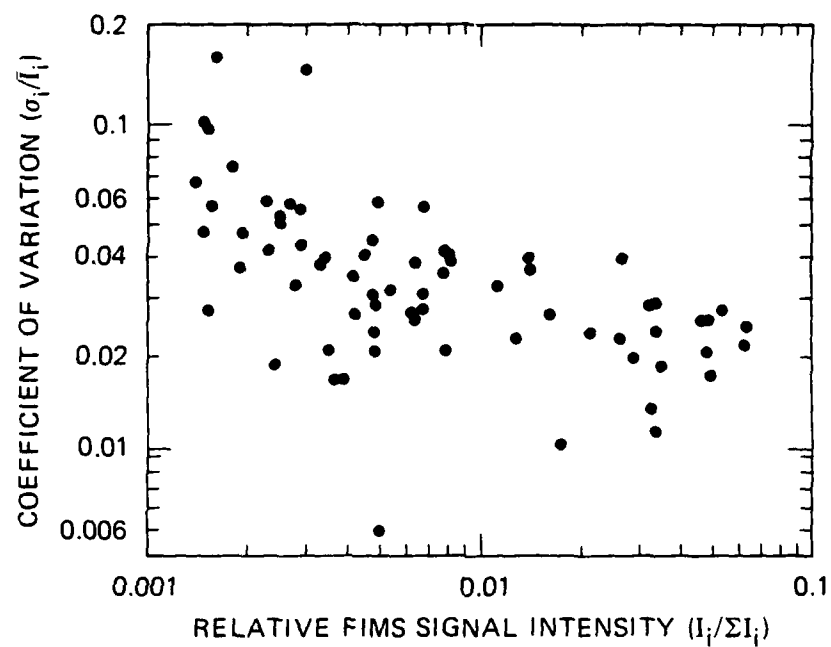
The main effect of the glass beads appears to be an increase in the forces which hold the sample molecules to the probe, thus requiring a higher temperature to vaporize the sample. This effect probably results from the very large surface area of the microporous beads. Most sample molecules are absorbed directly onto a glass surface rather than being part of a microscopic drop of liquid. Thus the energy required to remove a molecule of hydrocarbon from the solid to the gas phase is the binding energy between the molecule and the glass surface, rather than the apparently lower heat vaporization. This explanation also accounts for the tailing of peaks to lower temperatures seen in Figure 10 and for the relatively broader peaks in the temperature versus signal intensity plots. The tailing is due to a fraction of the hydrocarbon sample which was not adsorbed onto the glass beads as strongly as the majority of the molecules. The wide temperature range over which the sample evolved is due to a range of binding energies between the glass surface and the sample molecules.

Use of the microporous glass beads increases the convenience of obtaining FI mass spectra of volatile mixtures, because the temperature at which they evolved into the ion source is increased. However, there is no increase in the obtainable separation between compounds with similar boiling points. We, therefore, conclude that it will not be practical to use probe distillation procedures to separate middle distillate fuel components such as naphthalenes and saturates.

PRECISION OF FIMS ANALYSIS OF DISTILLATE FUELS

Our earlier work in the field ionization mass spectrometric analysis of distillate fuels was carried out by introducing the fuel sample into the mass spectrometer via the solids probe, as described above. When using the solids probe to introduce volatile samples, there is always the possibility of some unavoidable and variable loss of the most volatile components. This potential problem is avoided by using the glass batch inlet system. In order to determine the degree of precision to be expected from analyses of distillate fuels using the batch inlet system combined with FIMS, we carried out 5 replicate analyses of a jet fuel sample designated J-2 supplied to us earlier by the Naval Research Laboratory. For each analysis, 5 microliters of fuel were injected into the glass batch inlet system operated at 150°C. A total of 10 spectra were collected and averaged for each analysis.

The precision of the 5 analyses of fuel J-2 is shown by the data plotted in Figure 11 which shows the coefficient of variation of each peak as a function of the relative peak intensity. The coefficient of variation is defined as the standard deviation for a peak intensity divided by the average peak intensity. The relative signal intensity is just the intensity of a single peak divided by the sum of the intensities of all of the peaks in the FI mass spectrum of the sample. In this particular case, we considered only peaks which contained a minimum of 400 ions. The standard deviation due to counting statistics alone is the square root of the number of counts in a peak. For a peak containing 400 ions, the standard deviation is 20, corresponding to a coefficient of variation of 0.05 due to statistics alone. Any other random errors



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FIGURE 11 COEFFICIENT OF VARIATION VERSUS RELATIVE FIMS SIGNAL INTENSITY FOR JET FUEL SAMPLE J-2 RUN IN THE GLASS BATCH INLET

introduced by the mass spectrometer, batch inlet system, or data system would increase the average coefficient variation above this level.

Figure 11 shows that the coefficient of variation for the smallest peaks is indeed about 6%, and it drops to an average of between 2 and 3% for the largest peaks. On the basis of these results, we can project an accuracy of better than 10% for the quantitation of individual components in a distillate fuel sample analyzed via FIMS using a batch inlet system.

HIGH RESOLUTION FIELD IONIZATION MASS SPECTROMETRY

A mass spectrometer resolving power of 3,200 is required to separate the molecular ions of all of the possible hydrocarbon species which might be present in a middle distillate fuel. Compound classes such as naphthalenes and saturates, or cycloalkanes and biphenyls, which have the same nominal molecular weight but different chemical formulas, can be separated at this resolving power. Thus a field ionization mass spectrometer capable of operating at a mass resolution of 3200 or higher and equipped with a suitable batch inlet system and computerized data system would be capable of providing a detailed analysis and quantitation of the various hydrocarbon types present in a middle distillate fuel.

It was originally planned to add an electric sector to SRI's existing 90° magnetic sector mass spectrometer, thereby converting it into a double focusing high resolution instrument. In the course of this project, we decided that it would be more desirable to purchase a used high resolution mass spectrometer and adapt it for field ionization work. There were two reasons for this decision. First, our careful examination of the focusing properties of the magnetic sector in our existing mass spectrometer showed that the ions were not well focused at the detector slit. Because this mass spectrometer routinely operates at a resolution of only 500, the imperfection in the magnetic sector is hardly noticeable. However, in order to achieve high resolution and true double focusing operation, a new set of magnet pole pieces would be required. This would entail the complete rebuilding of the mass spectrometer magnet as well as the design and construction of a new electric

sector. We estimated that the cost to carry out such an extensive construction project would exceed the cost of purchasing and refurbishing a used commercial double focusing mass spectrometer.

The second reason for choosing to purchase a used high resolution mass spectrometer was the possibility of obtaining substantially higher mass resolution. Fifteen years ago, the mass resolution of high performance commercial mass spectrometers was usually limited by the stability of the electronics then available. Even so, mass resolutions of 40,000 up to 60,000 and even higher were obtained. The market value of a 15 year old high performance mass spectrometer is very small however because very few laboratories have the facilities and experience to restore them to good operating condition. Because there is very little that can go wrong with the electric and magnetic sectors on a mass spectrometer, it is almost always failures in the electronics which cause an expensive high performance mass spectrometer to deteriorate and eventually fall into disuse. Because we already have most of the electronics required to operate a field ionization mass spectrometer, the purchase of a used high resolution mass spectrometer offered the possibility of obtaining a superior magnetic and electric sector which could be converted to a field ionization instrument operating at a resolving power of 40,000 or better.

Permission has been obtained from the contract officer to purchase a used high resolution mass spectrometer. On the basis of its design and its demonstrated high resolution capability, we have selected the M.S.9 Mass Spectrometer manufactured by Associated Electrical Industries Limited as our first choice. The high stability version of this instrument has achieved resolving powers in excess of 70,000 and instruments with less sophisticated electronics have operated at resolving powers at 40,000 and greater. The electric and magnetic sectors of this mass

spectrometer are very similar to those of the M.S.50, a state of the art high resolution mass spectrometer currently manufactured by AEI. A notice announcing our interest in purchasing a used instrument was posted during the 28th Annual Conference on Mass Spectrometry and Allied Topics sponsored by the American Society for Mass Spectrometry and held May 25-30, 1980, in New York City. We have also placed advertisements in Chemical and Engineering News, the weekly magazine of the American Chemical society. Four different M.S.9 Mass Spectrometers have been located which may be available for sale. Negotiations are currently under way to select the instrument available in good condition at the best price.

When the used M.S.9 Mass Spectrometer arrives at SRI, it will be completely disassembled, cleaned, repaired, and reassembled in a like-new condition. If possible, we would like to test its resolution and sensitivity in its original electron impact configuration. However, if the original electronics require extensive reworking in order to do this, we will go immediately to the installation of an SRI volcano style field ionization source. We anticipate that we will be able to obtain a resolving power of approximately 40,000 while operating the mass spectrometer with the FI source. This level of resolution may not be reached immediately however. The initial resolving power may well be as low as 10,000 although it is difficult to imagine any uncorrectable conditions which could cause it to be any lower.

The ability to separate, detect, and quantitate minor components of the fuel containing the heteroatoms oxygen, nitrogen, and sulfur will depend on the mass spectrometer resolving power. Table 7 shows the resolving power required to separate possible mass doublets at m/z 300, the molecular weight of the heaviest components expected in middle distillate fuels. These mass doublets were selected as those most likely to be encountered in a field ionization mass spectrum, which consists of

Table 7

RESOLVING POWER REQUIRED TO SEPARATE POSSIBLE
MASS DOUBLETS AT m/z 300

<u>Mass Doublet</u>	<u>$\Delta M \times 1000$</u>	<u>Required Resolving Power at m/z 300</u>
C - H ₁₂	93.9	3,200
S - C ₂ H ₈	90.6	3,300
O - CH ₄	36.4	8,200
N ₂ - C ₂ H ₄	25.1	11,900
³⁴ SH ₂ - C ₃	16.5	18,200
¹³ CO - N ₂ H	15.7	19,100
CO - N ₂	11.2	26,700
¹³ C ₂ - C ₂ H ₂	8.9	33,600
N - ¹³ CH	8.11	37,000
C ₃ - SH ₄	3.37	89,000

unfragmented molecular ions. The doublets are listed in decreasing order of mass difference, or increasing values of the resolving power required to separate them. The carbon- $H_{1,2}$ doublet is the easiest to separate and requires only 3200 resolving power at mass 300. The separation of sulfur from C_2H_8 is only slightly more difficult requiring a resolving power of 3300. However, there is another doublet involving sulfur which is much more difficult to separate. The last entry in the table shows that a resolving power of 89,000 is required to separate the C_3-SH_4 doublet. This doublet can only occur in hydrogen deficient systems, and we do not anticipate that it will be very common in the extensively hydrogenated middle distillate fuels prepared from shale oil. However, the corresponding doublet for the sulfur-34 isotope can be separated at only 18,200 resolving power. Because sulfur-34 is present at the level of 4.2% natural abundance, there is at least the possibility of detecting major sulfur components from the presence of this isotope peak. There is little chance that a resolving power of 89,000 will be obtained in the foreseeable future with the high resolution FIMS.

Nitrogen is the most abundant and most important heteroatom found in refined middle distillate fuels from shale. In a molecular ion spectrum, the doublet which will be encountered is the $N-^{13}CH$ doublet which requires 37,000 resolving power to separate at m/z 300. The ability to resolve this doublet and thus detect and quantitate nitrogen containing compounds in whole fuel samples was a major factor in our decision to seek a high resolution capability.

In order to use the high resolution capability efficiently and effectively to analyze middle distillate fuel samples, a computerized mass spectrometer data system is essential. The data system presently available at SRI was designed for low resolution work and cannot readily be expanded to handle data obtained at resolving powers above 3000.

Although we could design, assemble, program and test a high resolution data system for the field ionization mass spectrometer, it would be less costly to purchase a commercial system. This would also make it possible for us to begin work much sooner on the computer programs needed to convert the raw data of the exact masses and intensities of the many hundreds of components present in a distillate fuel into a more useful table of the amounts of the various compound classes present in the fuel.

CONCLUSIONS

The combination of high resolution FIMS together with a batch inlet system appears to be a highly promising method for obtaining quantitative data on the chemical composition of middle distillate fuels. The precision obtained in the trial run using the existing low resolution FIMS instrument is quite good. Relative field ionization signal intensities can be converted into relative molar concentrations using data such as that obtained in this study on relative field ionization sensitivities. Our finding that minor components such as naphthalenes and compounds containing sulfur and nitrogen have relatively high field ionization sensitivities is fortunate, since it will enable us to quantitate these materials at lower levels than would otherwise be possible. A high resolution mass spectrometer operating at 40,000 resolving power will allow the separation of all molecular ions containing nitrogen and oxygen from hydrocarbon ions, and will separate those molecular ions containing sulfur from the expected hydrocarbon species.

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